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ULTRA-VIOLET BANDS OF ZINC IODIDE—PART III.

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Plate III

ABSTRACT. The band system E of the zinc iodide molecule, lying between λλ2450-2250 is photographed on the Hilger Littrow quartz spectrograph. Each band consists of three component heads, which are shown to be due to the three isotopic molecules $Zn^{64}I^{127}$, $Zn^{66}I^{127}$ and $Zn^{68}I^{127}$, thus confirming the existence of the isotope 68 of zinc for the first time from the study of bands. Vibrational analysis of the bands gave the following constants, for $Zn^{64}I^{127}$.

$$\nu = 44114.5 \qquad \begin{matrix}\omega' = 142.0 \\ \omega'' = 225.6\end{matrix} \qquad \begin{matrix}x'\omega' = 3.0 \\ x''\omega'' = 1.0\end{matrix}$$

The diffuseness of the bands with $v' > 2$ is considered as evidence of predissociation in the upper state between the vibrational levels $v' = 2$ and $v' = 3$.

INTRODUCTION

The emission spectrum of zinc iodide was investigated by Wieland (1929) along with other allied halides. He gave the analysis of an intense and violet-degarded system lying between λλ 3392.6-3257.8 and derived the vibrational constants

$$\nu = 30117.6 \qquad \begin{matrix}\omega' = 218.2 \\ \omega'' = 223.4\end{matrix} \qquad \begin{matrix}x'\omega' = 0.70 \\ x''\omega'' = 0.75\end{matrix}$$

In addition, he reported the existence of two more groups of bands, one in the vicinity of 2400A and the other in the visible; but no measurements were given. Later, Oeser (1935) studied the spectra of the halides of zinc and cadmium both in absorption and in fluorescence. He could not obtain any banded absorption for zinc iodide but listed about fourteen fluorescence bands in the visible region. In an attempt to find the second component of the Wieland system, which was suggested by Howell (1943) to be one component of a doublet electronic system due to the transition $^2\pi - {}^2\Sigma$, Tiruvenganna Rao and K. R. Rao (1946) reinvestigated the spectrum of zinc iodide in emission and established the predicted component system in the set of ten diffuse bands lying to the violet side of the Wieland's main system, with the upper state constants $\omega' = 211.7$, $x'\omega'' = 2.5$ and $\nu_e = 30506.3$.

The doublet width of 370 cm.$^{-1}$ so obtained is of the expected magnitude. They also confirmed the existence of bands in the λ2400 region and designated them as system E. The present paper deals with a detailed study of this system E.

EXPERIMENTAL

The experimental set up for this investigation is the same as that previously employed by the author in similar investigations and described in detail elsewhere. The spectrum is excited in the electrodeless H. F. discharge and also by a 1/4 K. W. transformer. For a complete development of this system E, it is found that the excitation with an H. F. oscillator is more favourable than that with a high voltage transformer. Considerable difficulty was experienced in obtaining a good photograph of the bands, due to the general continuum overlying the entire spectrum of the molecule. The system C between λλ3400-3250, analysed by Wieland, is the one most readily obtained owing to its high intrinsic intensity. A study of the various conditions in the discharge tube indicated that the overlapping continuum is probably not wholly due to the zinc iodide molecule itself, but most of it may be due to the continuous spectrum of free iodine (Ramasastry, 1947) formed as a decomposition product. After a number of attempts, it was found that the continuous spectrum could be reduced to a minimum and bands are brought out prominently by using the salt in a pure and dry condition, with optimum heating and minimum exposure in a very sharply focussed spectrograph having a fine slit. The colour of the discharge is beautiful golden yellow due, perhaps, to an emission continuum in the yellow region of the spectrum. The tube is to be heated until the salt just begins to sublime and the discharge shows this characteristic yellow colour To maintain the temperature, intermittent heating is essential, chiefly, just at the instants when the discharge shows a tendency to become less yellow and more white, for this condition represents an excessive partial vapour pressure of iodine. Initially, the tube gives some trouble because of the presence of traces moisture that are invariably present in the salt owing to the highly hygroscopic nature of zinc halides. When long exposures of about four hours duration are required, heating should be done more systematically, say for about 1½ seconds in every 5 seconds.

The Hilger small, medium and Littrow quartz spectrographs of dispersions of 15, 5 and 2 A.U. per mm. in this region are employed for photographing the bands. Ilford Special Rapid and Selo-Chrome plates are used. Some of the plates are sensitised with fluorescent oil. The system could be obtained practically with no continuous spectrum within about 5 minutes, 20 minutes and 3 to 4 hours respectively on the three instruments. Measurements are made with a Hilger comparator taking the iron arc lines as standards.

ANALYSIS

An examination of the spectrogram revealed that each band is not single but consisted of just three heads of decreasing intensity ; the fainter components occurring on the short wave-length side of the strongest or the main head. The relative intensities of the three heads, as estimated visually, remained almost the same from band to band. This has led to the consideration that the component heads are, prabably, of isotopic origin rather than details of rotational structure. Reference to the table of isotopes showed an agreement between the relative percentage abundance (50.9, 27.3, 17.4) of the three isotopes 64, 66, and 68 of zinc and the estimated ratio of the intensities of the three component heads. The three components are thus attributed to the isotopes of zinc as iodine, the other constituent of the molecule is known to have but a single isotope of mass number 127. Keeping this feature in view, the vibrational analysis is worked out. The picture (Plate III b) presents prominently four pairs of intense bands with sharp heads between $\lambda 2359$ and $\lambda 2327$. The wave-number differences between corresponding members of adjacent pairs are about 215 cm^{-1} which is of the order of the ground state frequency ($\omega'' = 223.4$) and it gradually decreases as one goes towards the longer wave-length side. Considering these successive members as forming ground state progressions, they could be extended both ways to include as many as twelve members in each ; the intensity in each progression rises to a maximum and then falls off gradually, as is expected. The appearance of distinct pairs, however, does not continue (Plate III a) very far. As the long wave-length end is approached, a sufficiently intense band is found to occur between the pairs. These intermittent bands, about six in number, could be formed into a third ground state progression with a smaller value of v'. Almost all the intense band heads in this manner formed members of three v'' progressions with $v' = 0$, 1 and 2. About a dozen bands towards the violet end, which are bread, diffuse and faint, have alone remained to be classified. The measurement of these bands is uncertain by as much as 0.5 A. U. corresponding to about 10 wave-numbers in this region. The very diffuse nature of these bands suggests the setting-in of predissociation in the upper state after the vibrational level $v' = 2$. On this basis they could be grouped into two progressions with $v' = 3$ and $v' = 4$. The uncertainty in the measurements of these bands on account of their diffuseness may be expected to account for the large discrepancies in the $\Delta G (v)$ values. The vibrational scheme thus derived is presented in Table I.

Table II gives details of the wave-length, wave number data of the bands. The last column gives the assignment. The measurements are the mean values of four independent settings on the medium as well as Littrow Hilger quartz instruments. The symbol M indicates measurements only on the medium quartz plates. The intensities are visual estimates.

TABLE I

ZnI Bands—Vibrational Analysis of the E-System

v″ \ v′	0	1	2	3	4	ΔG(v)
0				—	—	
1				44254 (0)	44391 (0)	
2		43773 (1)	43883 (1)	44039 (1)	44170 (1)	
3		43336.5 (1)	43672 (1)	43823 (2)	43954 (2)	
4		43336.5 (1)	43169.5 (2)	43598 (2)	43737 (1)	
5		43118.5 (2)	43242.5 (2)	43382.5 (1)	43514 (1)	217.5
6		42902.5 (3)	43028.5 (3)	—	43297 (1)	215.9
7	42540.5 (1)	42688.0 (5)	42816.0 (2)	42955.3 (1)	43082.0 (0)	213.3
8	42329.5 (2)	42476.5 (5)	42605.0 (3)	42731.5 (1)	42868.0 (0)	211.5
9	42126.0 (4)	42267.0 (4)	42398.5 (4)	42522.0 (1)	42652.5 (0)	206.8
10	41924.5 (4)	42060.0 (4)	42192.0 (4)			205.0
11	41723.5 (1)	41852.0 (3)	41986.5 (3)			204.8
12	41525.5 (2)	41646.5 (2)	41783.5 (2			202.2
13	41332.0 (0)	—	41580.5 (2)			195.7
14	—	—	41380.0 (1)			—
15	40927.0 (0)	41059.0 (1)	41181.5 (0)			200.5
16	40734.0 (0)	40872.5 (1)				
ΔG(v)	136.0	130.0				

TABLE II

Zinc Iodide Bands—System E

Wave-length	Int.	Wave-number	Assignment	
			(v′.v″)	Zn Isotope
2458.05	0	40670.0M	(1,17)	64
2454.2	0	40734.0M	(0,16)	64
2445.9	1	40872.5M	(1,16)	64
44.7	0	892.5M		
2442.65	0	40927.0M	(0,15)	64
2434.80	1	41059.0M	(1,15)	64

TABLE II (*contd.*)

Wave-length	Inst.	Wave-number	Assignment (v', v'')	Assignment Zn Isotope
2427·55	0	41181.5	(2,15)	64
2426.6		41197.0		
2425·4		41217·5		
2418.7	0	41332.0	(0,13)	64
2417.85	0	41346.0		
2415·9	1	41380.0	(2,14)	64
14 3	0	406.5		66
13.7	0	418.0M		67 ?
13.0	0	430.0M		68
2410.9	1	41466 0	(1,12) ?	64
2410.05	0	41480.5		
2407.45	2	41525.5	(0,12)	64
05.58	1	552·5		66
			(0,12)	68
2404.25	2	41580.3	(2,13)	64
02 65	0	607.5		66
01.45	0	629.0		68
2400.45	2	41646.5	(1,12)	64
399.5	1	662.5		66
98.1	0	687.0M		68
2396.0	1	41723.5	(0,11)	64
94.45	0	750.5		65
93.35	0	761.0		67 ?
93.05	0	775.0		68
2392.55	2	41783.5	(2,12)	64
91.3	1	805.0		66
90.1	0	826.0		68
2388.65	3	41852.0	(1,11)	64
88.2	0	860.0		
87.35	1	874.5		66
86.7	0	886.0		67
86.0	0	898.0		68
2385.1	0	41914.5		
2384.5	4	41924.5	(0,10)	64
83.1	2	949.0		66
81.85	0	971 5		
2381.0	3	41986.5	(2,11)	64
79.85	1	2007.0		66
78.65	0	028.0		68
2376.85	4	42060.0	(1,10)	64
75·75	2	079.0		66
74·75	1	097.0		68
2373.1	4	42126.0	(0,9)	64
71·75	2	150.5		66
70.5	0	171.5		68

TABLE II (*contd.*)

Wave-length	Int.	Wave-number	Assignment	
			(v′ v″)	Zn Isotope
2369 4	4	42192.0	(2,10)	64
68.4	2	210 0		66
67.95	0	217 5		67
66.85	1	237 0		68
2365.2	4	42267.0	(1,9)	64
64.1	2	286.0		66
63.1	1	304 5		68
2361 7	2	42329 5	(0,8)	64
60.5	1	350.5		66
59 86	0	362 5		67
59.9	1	378.5		68
2357.85	4	42398.5	(2,9)	64
56.7	2	419.5		66
56.2	0	428.5M		67
55,6	1	439.0		68
2353.5	5	42476.5	(1,8)	64
52 6	3	493.5		66
51 65	1	510.0		68
2351.0	od	42522 0	(3,9)	64
50.3	od	534.5		
2350.0	1	42540.5	(0,7)	64
47.9	0	577.0		68
2346 4	3	42605.0	(2,8)	64
45 3	1	625 0		66
44 0	0	642.5		68
2343.8	od	42652.5	(4,9)	64
42.9	od	667.5		
2341.9	5	42688.0	(1,7)	64
41.0	2	705 0		66
40.2	1	718 0		68
2339.5	1	42731.5	(3,8)	
38.9	0	752		
38 0	0	758.5		
2334.85	2	42816.0	(2 7)	64
33 90	1	834.0		66
32 95	0	851.0		68
2332 00	0	42868.0	(4,8)	
31.20	0	883.0		
2330.15	3	42902.5	(1,6)	64
29 35	2	916.5		66
28.75	1	927.5		68
2327.35	1	42953 5	(3,7)	64
26.55	0	568.5		
25.95	1	980.5		

TABLE II (*contd.*)

Wave-length	Int.	Wave number	Assignment	
			(v′, v″)	Zn Isotope
2323 3	3	43028.5	(2,6)	64
22.55	2	04 .5M		66
21.95	1	057 5		68
2320 45	1	4308. 0	(1,7)	
19 40	0	108 0		
2318 5	2	43118.5	(1,5)	64
17.9	1	129.0		66
17.5	0	136.0		68
2311 95	2	43242 5	(2,5)	64
11 3	1	25?.0		66
10.85	0	260 5		68
2308 9	1	13297 0M	(4,6)	
07 35	1	326 5		
2306.8	1	43336.5	(1,4)	64
05.9	0	351.0		66
2304.35	1	43382.5	(3,5)	
03 8	0	393 5		
03 1	0	405 5		
2300 1	0	43463M		
2299.75	2	43469 5	(2,4)	64
99.3	1	478 9		66
2297.4	1	43514M	(4,5)	
2295 5	1	43550 M	(1,3)	
2293 0	2	43598 M	(3,4)	
2289 1	1	43671 M	(2,3)	
2285 7	1	43737 M	(1,4)	
2283 8	1	43773	(1,2)	
2281 2	2	43823 M	(3,3)	
2278 1	1	43883 M	(2,2)	
2274 4	2	43954 M	(1,3)	
2270 0	1	44039 M	(3,2)	
2263 3	1	44170 M	(1,2)	
2259 0	0	44254 M	(3,1)	
2252.0	0	44391 M	(4,1)	

The vibrational constants for the upper states had to be determined only from the two intervals 136 and 130 involving the levels $v'=0$, 1, and 2. Examination of the data indicates that even of these two values o

(130) is reliable. The difference 136 is obtained as a mean of about eight values which show large discrepancies. It may be significant to note that there is a steady decrease in the values, probably it arises from errors involved when the band heads instead of the band origins had to be measured. On account of such discrepancies the adopted values $\omega' = 142$, $x'\omega' = 3.0$ should be considered only as approximate.

For the determination of the constants of the ground state a graphical method is employed. The differences formed from bands, on which the settings are doubtful, are discarded. Averages of the remaining reliable $\Delta G(v)$ values are plotted as ordinates against equal divisions on the abscissae and a curve is drawn (Fig. 1) passing through as many points as possible. By extrapolation the ω'' value of 223.9 is obtained which agrees with the

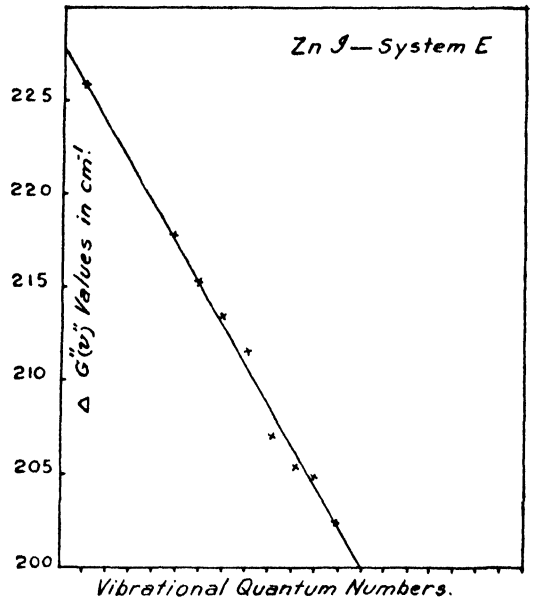


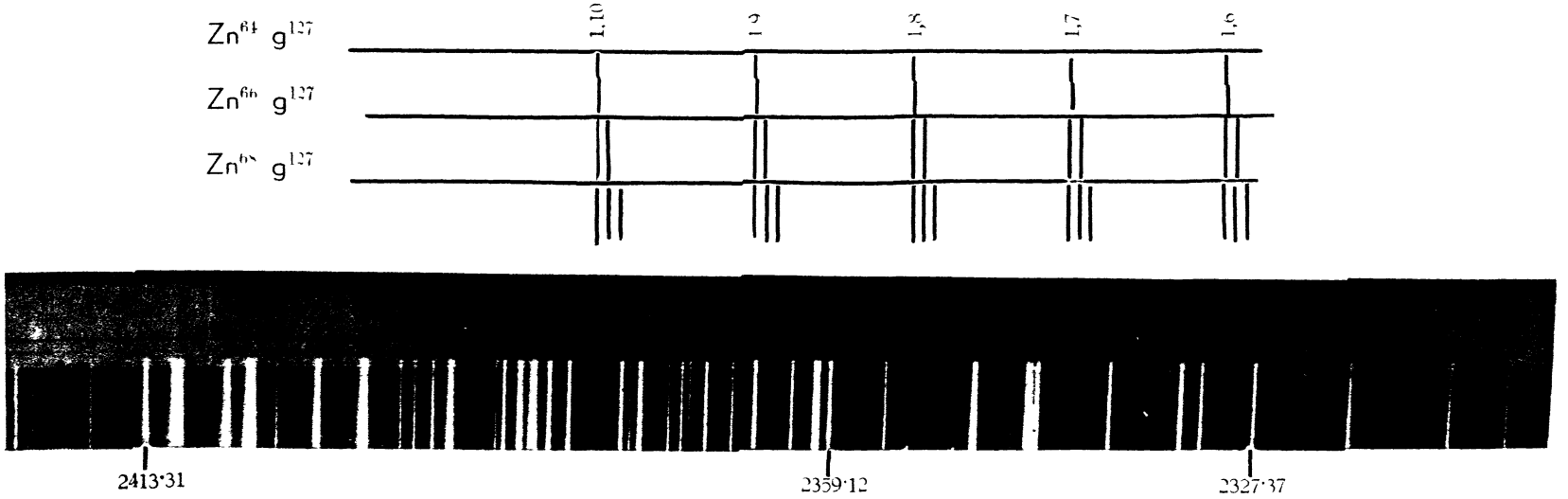
FIG. 1

value 223.4 reported previously by Wieland and is consistent with the view that all the v'' vibrational levels, beginning from $v'' = 0$, are represented among the bands, *i.e.*, starting with the assignment of the two bands of wave-numbers 44254 and 44391 as (0,3) and (0,4) bands respectively.

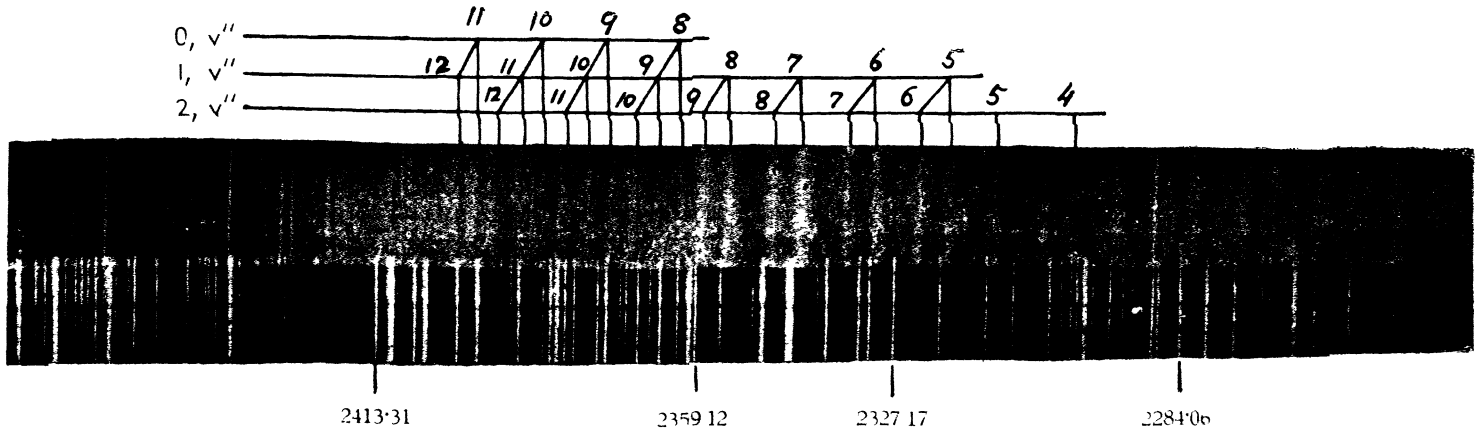
With the above vibrational constants and the quantum number assignments a confirmation of the scheme is attempted with the help of the isotope shifts. This has revealed a systematic divergence between the calculated and the observed isotopic shifts. A satisfactory agreement could finally be arrived at when the ground state vibrational quantum numbers are increased by 1. It meant starting with the assignment of the two bands $v44254$ and $v44391$ as (1,3) and (1,4) instead of as (0,3) and (0,4) respectively; this also involved an increase in the value of ω'' from 223.9 to 225.6. Though there will be no

Fig. 4. Zinc Iodide Bands (E System).

(*a*) Medium Quartz and (*b*) Quartz Littrow Spectrograms



(*b*)



(*a*)

bands to represent the $v''=0$ level, it is this assignment of quantum numbers that is finally adopted and is shown in Tables I and II. The agreement between the observed and calculated isotope shifts in the case of all bands, where the measurements could be made with some degree of certainty, is seen from Table III and Table IV is a collection of all the constants used in the calculation.

TABLE III (*Isotopic Shifts*)

v'' / v'	0		1		2	
	obs.	cal	obs	cal	obs.	cal.
4					8.5	7.3
					—	14.6
5			10.5	11.1	9 5	9 6
			17 5	22 2	18.0	19 2
6			14 0	13 6	14 0	12.1
			29 0	27 2	29 0	24 2
7	—	17 3	17.0	16 0	18 0	14.5
	36 5	34 0	30 0	32 0	35 0	29.0
8	21 0	19 8	17.0	18.5	20.0	17.0
	-	39.6	33 5	37.0	37.5	34.0
9	24.5	22.1	19 0	20 8	21 0	19 3
	45 5	44 2	37 5	41.6	40 5	38.6
10	24 5	24.5	19 0	23 2	18.0	21.8
	—	49.0	37 0	46 4	45 5	43 6
11	27 0	27 0	22.5	25 7	20 5	24.2
	51 5	54 0	46.0	51 4	41 5	48.4
12	27 0	29.4	—	28.1	21.5	26.7
	55 0	58 8	40.5	56 2	42.5	53 4

TABLE IV

$\nu_e = 44114.5$

$\omega'_e = 142.0$ $\omega_e'' = 225.6$

$x'_e\omega'_e = 3\ 0$ $x''_e\omega' = 1.0$

Molecule	$\rho-1$	ρ^2-1
$Zn^{66}\ I^{127}$	— 01	— 02
$Zn^{68}\ I^{127}$	—.02	— 04

Three characteristic features of this system of zinc iodide bands may be emphasised in conclusion, which are not observed in the system C, analysed by Wieland.

(*a*) For the first time, evidence of the isotopes of zinc 66, 68 (and probably also of 67) has been distinctly obtained. The relative magnitudes of the ω' and ω'', the large v'' values involved in the band system, and the direction of degradation of the bands proved favourable for the detection of the isotopic

components, whereas in the C-system the isotopic heads corresponding to mass 66 only are resolved.

(*b*) Predissociation in the upper electronic state which is in evidence not by an abrupt absence but by the sudden diffuseness of all the bands after the vibrational level, $v'=2$.

(*c*) Long ground state progressions, rather than long sequences while the sequence appears, are predominent on the C-system.

All these features are found also in yet another system of the zinc iodide which the author has succeeded in photographing. This system (which may be designated as D_1) was not measured or even mentioned by any of the previous workers. It consists of about eighty bands between $\lambda 3000$ and $\lambda 2700$. The bands are degraded to the red. A preliminary analysis gave two long progressions but the presence of a third one could not as yet be established definitely owing to the crowding and considerable overlapping of the main heads and the isotopic heads. The analysis of this system of bands will be presented in a later communication.

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REFERENCES

Howell, 1943, *Proc. Roy Soc.*, **182**, 95.
Oeser, 1935, *Zeit. f. Phys.*, **95**, 699.
Ramasastry, 1947, *Ind. J. Phys.*, Communicated.
Tiruvenganna Rao and K R Rao, 1946, *Ind. J. Phys.*, **20**, 49.
Wieland, 1929, *Helv. Phys. Acta.*, **2**, 46 and 77.